

AD-A176 172

APPLICATIONS OF THERMAL MODULATION IN LUMINESCENCE  
SPECTROSCOPY(U) WASHINGTON STATE UNIV PULLMAN DEPT OF  
CHEMISTRY G A CROSBY ET AL JAN 87 TR-5

1/1

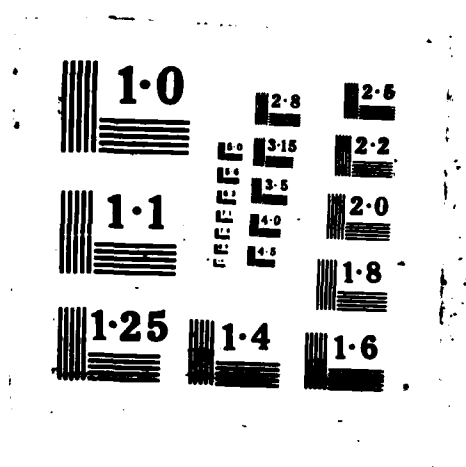
UNCLASSIFIED

N00014-83-K-0609

F/G 7/4

NL





UNCLASSIFIED

(12)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ONR-TR-5	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Applications of Thermal Modulation in Luminescence Spectroscopy		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
		6. PERFORMING ORG. REPORT NUMBER
AUTHOR(s) G. A. Crosby and K. J. Jordan		8. CONTRACT OR GRANT NUMBER(s) N00014-83-K-0609
PERFORMING ORGANIZATION NAME AND ADDRESS Washington State University Chemical Physics Program/Department of Chemistry Pullman, WA 99164-4630		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 051-848 (01d) R & T Code N63374
CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 North Quincy Street Arlington, VA 22217		12. REPORT DATE January 1987
		13. NUMBER OF PAGES 5
MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report)  Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)  <div style="text-align: right;"> <b>DTIC</b>  <b>ELECTE</b>  <b>S</b> JAN 27 1987 <b>D</b> </div>		
18. SUPPLEMENTARY NOTES  To be published in Proceedings of the Conference on Fluorescence Detection, International Society for Optical Engineering (Los Angeles Meeting, Jan 1987), Vol. 743.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  Thermal Modulation Luminescence Excited States Infrared Heating Metal Complexes		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  The utility of thermally modulated emission (TME) spectroscopy as a technique for elucidating the properties of the excited states of molecules and complexes with near-degenerate excited electronic states is reviewed. A description of the TME method, its realm of application, and the type of information obtained are given. Particular emphasis is placed on the use of infrared heating as a tool for observing spectra in diverse media. Keywords:		

DD FORM 1473  
1 JAN 73

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

AD-A176 172

DTIC FILE COPY

OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0609

R & T Code N63374  
(Old Task No. NR 051-848)

TECHNICAL REPORT NO. 5

Applications of Thermal Modulation in Luminescence Spectroscopy

by

G. A. Crosby and K. J. Jordan

Prepared for Publication

in

Proceedings of Conference on Fluorescence Detection  
International Society for Optical Engineering  
(Los Angeles Meeting, Jan 1987), Vol. 743

Washington State University  
Department of Chemistry  
Pullman, WA 99164-4620

January 15, 1987

Reproduction in whole or in part is permitted for  
any purpose of the United States Government

This document has been approved for public release  
and sale; its distribution is unlimited.

Applications of thermal modulation in luminescence spectroscopy

G. A. Crosby and K. J. Jordan

Department of Chemistry and Chemical Physics Program, Washington State University  
Pullman, Washington 99164-4630

Abstract

The utility of thermally modulated emission (TME) spectroscopy as a technique for elucidating the properties of the excited states of molecules and complexes with near-degenerate excited electronic states is reviewed. A description of the TME method, its realm of application, and the type of information obtained are given. Particular emphasis is placed on the use of infrared heating as a tool for observing spectra in diverse media.

Introduction

Properties of the low-lying electronic excited states of metal complexes in condensed phases are most conveniently studied by monitoring the luminescence generated by UV excitation.<sup>1</sup> For most substances the parameters generally obtained are the energies of the emitting states above the ground state and the lifetimes of the excited states. Additional information can be obtained about the radiative and radiationless constants of the states if optical quantum yield measurements are carried out, although this determination can be tedious.<sup>2</sup>

If the emitting level in a luminescence experiment is nondegenerate, the interpretation of the luminescence results is usually unambiguous, since only one state is involved. Often, however, the 'state' is not a state at all but a group (usually three) of excited states in close proximity. If information is desired on the individual components of the 'state', then other experimental methods must be employed. For organic molecules the lowest excited triplet is a well-known example of a set of states that are closely packed, within a few  $\text{cm}^{-1}$ . The elucidation of the properties of the individual components can be effected by the use of Optically Detected Magnetic Resonance (ODMR) in which optical pumping is supplemented with microwave irradiation that pumps systems between the closely-lying components.<sup>3</sup> Since the splittings of the low-lying triplets of numerous molecules, including many metal complexes, lie in the region spanned by commercial microwave generators, the ODMR method has been used by numerous laboratories to measure properties of the individual triplet components.

For many metal complexes, particularly those of the second and third transition series, the lowest-lying excited states are only near-degenerate. Often the splittings range from a few wavenumbers to several hundred  $\text{cm}^{-1}$ , and ODMR cannot be used to stimulate transitions among them. The level splittings are in the frequency range of vibrations in solids and complex molecules, and tunable IR radiation would be required to effect transitions between the levels. Even if available, tunable IR radiation would be absorbed by the numerous vibrational modes present in the samples, and electronic transitions would be difficult to identify.

Recently we have been developing the technique of Thermal Modulation Emission (TME) spectroscopy to study the excited states of transition metal complexes. These complexes display photoluminescence from several excited states that are thermally accessible from the lowest one either by resistive heating or by direct IR heating. TME measurements supply complementary information on the excited state splittings in these molecules, information that is particularly difficult to obtain by other techniques because of the intrinsically diffuse nature of the emission spectra. The band widths are often orders of magnitude wider than the level splittings.

Description of the thermal modulation emission method

When a sample of a metal complex is held at low temperature and excited with UV radiation, broad band visible emission is frequently observed. Often the emission is a composite of bands originating from several excited states of the system and spans the entire near-UV and visible regions of the spectrum. Under steady excitation the emission band may display evidence of several transitions underlying it, but the contour is often uninformative. If, however, the sample is periodically heated while under constant UV irradiation, then three possible ideal behaviors of the emitted light are manifest. These are shown in Figure 1. In the figure we see that the intensity of a transition may increase, decrease, or remain constant as the sample is heated. Thus, a periodic signal possessing the frequency of the heat pulse will be superimposed on the steady-state

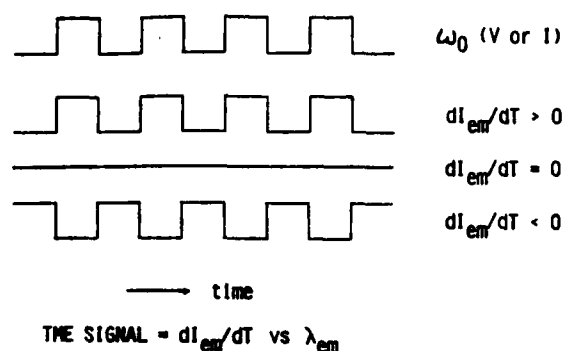


Figure 1. Schematic representation of ideal TME signals.  $\omega_0$  = frequency of heat pulse, joule or infrared radiation heating;  $(\partial I_{em}/\partial T)$  = derivative of emission intensity with temperature.

ODMR on an organic crystal system.<sup>6</sup> Later Hipps and Francis applied TME to inorganic compounds with near-degenerate excited states and showed the usefulness of TME for distinguishing between proposed excited state models.<sup>7</sup> With the introduction of several simplifying mathematical approximations these authors also derived expressions for the expected magnitude of the TME signal in the limit of small temperature excursions of the sample [for details see ref. 7]. For a lock-in amplifier properly phased and tuned to  $\omega_0$ , the TME output signal is

$$\Delta I \approx \frac{4(\bar{T} - T_b)}{\pi[1 + (\omega_0 \tau)^2]^{1/2}} \left( \frac{\partial I}{\partial T} \right)_{\bar{T}}$$

In this expression  $\omega_0$  is the frequency of the square wave heat pulse in the resistive heater attached to the sample;  $T_b$ , the temperature of the bath;  $\bar{T}$ , the average temperature of the sample, and  $(\partial I/\partial T)_{\bar{T}}$  is the temperature derivative of the band intensity.  $\tau$  is the thermal relaxation time of the sample. We see that the TME signal,  $\Delta I(\lambda)$ , is directly proportional to  $(\partial I/\partial T)_{\bar{T}}$  under these somewhat restrictive conditions. Ideal behavior of the emitted light is represented in Figure 1. In the real case the signal is not a step function; it is periodic, however, with a phase lag that is a complicated function of the heat conductivity of the sample.<sup>7</sup>

In the present work we are concerned with the development and refinement of TME spectroscopy as a technique for the investigation of the excited states of inorganic complexes. Particular emphasis is placed on the correspondence of the results obtained from different methods of heating the sample and the extension of the technique to the study of the same molecule in various solvent (glass) environments.

#### Description of experimental measurements

Both steady-state and TME spectra were recorded by illuminating the sample with filtered UV light from a mercury lamp and directing the emitted light through a monochromator supplied with UV blocking filters before the entrance slit. The signal from the photomultiplier detector was amplified and stored. The sample, usually a single crystal or a mass of crystals, was bonded with mineral oil to a thin-film nichrome heater and mounted in a variable temperature helium dewar. Cooling was achieved by suspending the sample just above the liquid helium reservoir.

For the TME measurements periodic temperature excursions within the sample were produced by driving the thin-film nichrome heater ( $R \sim 20$  ohms) with a square wave voltage oscillator of variable frequency, duty cycle, and pulse voltage. The oscillator was generally operated between 4 and 6 Hz to ensure optimal temperature excursions within the sample. Signal forms were insensitive to both the frequency and the duty cycle chosen. The AC component induced on the emission spectrum was detected by a properly phased lock-in amplifier whose output was amplified and recorded. Determination of the absolute sign of a given TME signal was accomplished by passing a single large-amplitude heat pulse through the sample and monitoring the sense of the phototube response with an electrometer.

Infrared heating of the samples was achieved by substituting a 10-W tungsten lamp and a mechanical chopper or a 4-W  $\text{CO}_2$  continuous wave laser for the resistive heater. The broad-

emission. It is not necessary that the emitting levels be in thermal equilibrium; nor is it necessary that all the levels be thermally accessible. What is necessary, however, is that the heat transfer to and from the sample be fast enough to produce reproducible temperature excursions at a frequency detectable by a lock-in amplifier. This condition is most easily achieved by mounting the sample on a resistive heater inside a low-temperature dewar that uses an exchange gas to conduct heat efficiently from the sample.

Although the thermal modulation (TM) technique had been employed in the measurement of reflectance spectra<sup>4</sup> and absorption spectra,<sup>5</sup> application of TM spectroscopy to luminescence measurements on molecular crystals was first introduced by Francis and coworkers, who demonstrated the equivalence of TME and

band output of the tungsten lamp was passed through a Corning 7-56 glass filter and focussed on the sample through the same window that transmitted the UV excitation beam. Since quartz windows are opaque at  $10.6 \mu$ , a modified optical arrangement was employed to direct the  $\text{CO}_2$  laser beam to the sample. In this case the sample was mounted at the bottom of a stainless steel tube that was equipped with a NaCl window at the top. The IR beam from the laser was routed by mirrors through the window down to the sample.

For the determinations employing IR pumping (the laser and the tungsten lamp) the sample excitation was essentially front surface. Excitation of glasses was achieved by cooling the block initially to 77 K, depositing a drop of solution into a depression on the block and quickly transferring the apparatus to the helium dewar. The power of the IR heating was estimated to be 150 mW by comparison of the recorded TME signals with those obtained by resistive heating.

### Results

Emission spectra of  $\text{Zn}(4\text{-Me-PhS})_2(\text{phen})^*$  crystals at 6.5 K are reproduced in Figure 2. In Figure 2a the steady-state luminescence is shown. Presented in 2b and 2c are TME spectra taken with resistive and IR laser heating, respectively. The data clearly reveal that the first spectrum is composed of at least two bands, a structured emission spanning the region of  $18,000$  to  $22,000 \text{ cm}^{-1}$  and an overlapping band almost devoid of structure that extends into the red region. The high energy band decreases in intensity as the temperature rises and the low energy one displays the opposite behavior. After flash excitation the former decays with a long life (0.34 s), whereas the latter dies out in milliseconds.<sup>8</sup> These ancillary transient measurements demonstrate that at least two excited states not in thermal equilibrium at the temperature of the steady-state experiment give rise to the observed emission. The TME results show conclusively that the high energy state loses intensity and the lower energy one gains intensity as a result of the heat pulse. Detailed studies on a similar molecule<sup>9</sup> lead to the inference that  $\text{Zn}(4\text{-Me-PhS})_2(\text{phen})$  has two excited states of widely disparate natures that are separated by a thermally accessible barrier. Each state decays independently at the temperature of the experiment until the relative populations are changed by the heat pulse. Systems are driven from the high energy (long-lived) state to the lower energy one thermally, thus producing a decrease of the intensity of the former and an increase of the intensity of the latter. A comparison of the curves in Figure 2a and 2b also shows that the TME results do not depend upon the method of heating. Indeed, a tungsten lamp can be substituted (see below) for the resistive heating source.

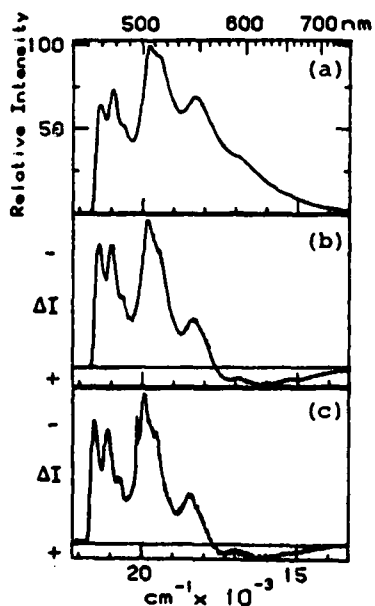


Figure 2. Emission spectra of  $\text{Zn}(4\text{-Me-PhS})_2(\text{phen})$  crystals at 6.5 K. (a) steady state; (b) thermally modulated by resistive heating at 5 Hz; (c) TME via  $\text{CO}_2$  laser at 4 Hz.

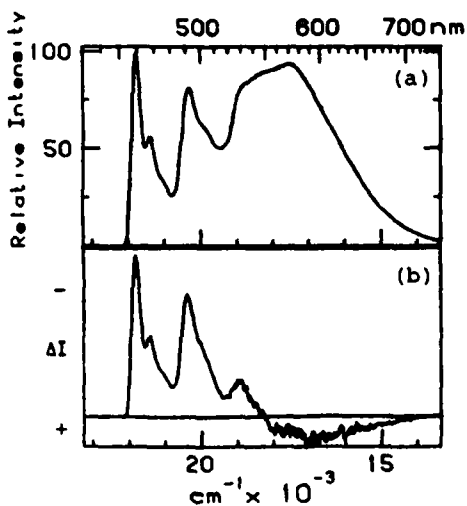


Figure 3. TME spectrum of  $\text{Zn}(\text{PhS})_2(2,9\text{-Me}_2\text{-phen})$  crystals at 6.5 K. (a) steady state emission; (b) heated with tungsten lamp at 4 Hz.

\* For names, abbreviations, and preparations of these zinc complexes, see ref. 8.

In Figure 3 we have plotted the TME signal from the  $\text{Zn(PhS)}_2(\text{phen})^*$  complex in the crystalline state at 6.5 K. In this experiment the heating element for the TME

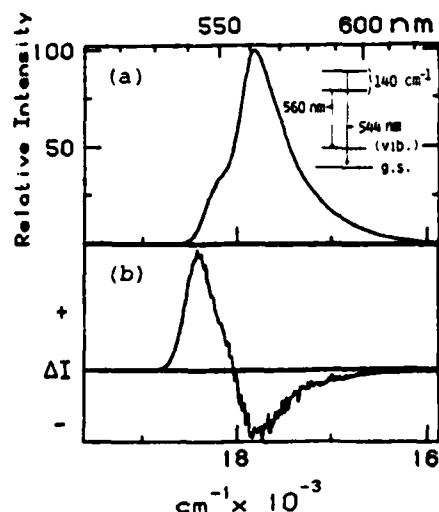


Figure 4. Emission spectra of  $[\text{Ir}(2=\text{phos})_2]\text{ClO}_4$  in 16:4:1 v/v ethanol/methanol/methylene chloride glass. (a) steady state at 6.5 K, insert displays published energy level system; (b) thermally modulated emission at 8.5 K via  $\text{CO}_2$  laser heating at 2 Hz.

measurement was a tungsten lamp whose radiation was directed into the dewar through a quartz window. The TME signal clearly reveals the composite nature of the steady-state spectrum. At least two electronic transitions occur under the band contour, a structured one lying at higher energies and a diffuse one at lower frequencies. This molecule also displays a barrier between the two emitting excited states that prevents thermal communication at 6.5 K. Thermal redistribution of the ensemble population is induced by the periodic heat pulses leading to the recorded TME spectra.

Figure 4 shows both the steady-state and the TME spectra of the open-shell complex  $[\text{Ir(III)}(2=\text{phos})_2]\text{ClO}_4^{**}$ . The normal spectrum is clearly composite since the TME curve shows both a positive and a negative intensity excursion as a function of the heat pulse. Unlike the two previous cases, however, the entire spectrum decays with a single life at all temperatures showing that the relative populations of the two emitting levels are controlled by the Boltzmann law.<sup>10</sup> No evidence for a barrier between the two emitting states is present but the TME signal is strong. Evidently the heat pulse redistributes the excited population continuously as the temperature changes. Another interesting feature of this experiment is the physical state of the sample. The complex was dissolved in a glass, rather than maintained in the crystalline state, thus allowing a TME signal to be obtained on a molecularly dispersed system.

#### Discussion

The results presented above show the power of TME spectroscopy as a tool for the study of inorganic complexes possessing near-degenerate excited states. Moreover, the results demonstrate that thermal equilibrium among the levels is not a prerequisite for obtaining TME signals. If a barrier separates the emitting levels, however, the magnitude of the heat pulse must be high enough to pump systems over it.

Resistive heating can be employed to generate TME signals, but several problems arise. Wires to the heater must be led into the dewar and attached to the heater, a tedious procedure. Also, attaching the sample to the heater by mineral oil is not always entirely satisfactory. Frequently the crystal pops off the heater when a large heat pulse is delivered to it at low temperatures. Finally, the resistive heating technique is limited by the rate of heat conduction to the sample from the heater, and we have devised no reliable method of measuring the amount of heat actually absorbed by the crystal during the heating cycle.

Employing an infrared radiative source to deliver heat to the crystal has several definite advantages over the use of resistive heating. Because the radiation is absorbed directly by the crystal, more uniform heating occurs. The limiting factor becomes the rate of dissipation of heat to the bath rather than the rate of heat conduction to the sample. This virtually dictates that an exchange gas must be present to cool the sample. Nonetheless, we have obtained TME signals from samples mounted in a displacer cryostat where no exchange gas was present. The slower cooling vitiated the TME signal and a lower frequency ( $\sim 1$  Hz) was required to produce any result. There was interfering scattered light from the tungsten lamp, which could have been, however, eliminated by interposing a silicon window to pass IR radiation of wavelengths longer than 1.1 microns (this filter was not available to us for taking the data presented here). Another advantage of IR heating is the ease of shaping the excitation pulse and modifying the duty cycle by means of simple choppers. A third, but extremely important, advantage of IR heating is the ease of working with samples dispersed in glasses, thus affording an opportunity for studying the effect of solvent matrix on the excited state properties. Finally, one can measure the absolute energy deposition rate in the samples by optical methods when an IR heating source is employed.

\*\* The name, synthesis, and a detailed spectroscopic investigation of  $[\text{Ir(III)}(2=\text{phos})_2]\text{ClO}_4$  are given in ref. 10.



Thermally modulated emission spectroscopy is a valuable tool for studying the properties of near-degenerate excited states of luminescent materials. Coupled with decay time, quantum yield, and conventional emission measurements, TME is providing new information on transition metal complexes of interest to spectroscopists and photochemists.

#### Acknowledgments

This research was supported by the National Science Foundation under Grant CHE-8421282 and the Office of Naval Research.

#### References

1. Crosby, G. A., "Spectroscopic Investigations of Excited States of Transition-Metal Complexes", Acc. Chem. Res., Vol. 8, pp. 231-238, 1975.
2. Demas, J. N.; Crosby, G. A., "The Measurement of Photoluminescence Quantum Yields. A Review", J. Phys. Chem., Vol. 75, pp. 991-1024 (1971).
3. El-Sayed, M. A., "The Triplet State: Its Radiative and Nonradiative Properties", Acc. Chem. Res., Vol. 1, 8-16, 1968.
4. Cardona, M., Modulation Spectroscopy, Academic Press, 1960.
5. Loh, E., "Thermally Modulated Absorption of  $\text{Fe}^{2+}$  Ions in Micas Vivianite and Olivine", J. Phys., Vol. C 5, pp. 1991-1998, 1972; Loh, E., "Thermally Modulated Absorption of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Mn}^{2+}$  in Spessartine and Almandine Garnets", Am. Mineral., Vol. 60, pp. 79-83, 1975.
6. Hunter, S. J.; Parker, H.; Francis, A. H., "Heat Pulse Modulation of Molecular Crystal Phosphorescence", J. Chem. Phys., Vol. 61, pp. 1390-1398, 1974.
7. Hipps, K. W.; Francis, A. H., "Thermal Modulation Spectroscopy Applied to Inorganic Compounds with Near Degenerate Excited States", J. Phys. Chem., Vol. 83, pp. 1879-1884, 1979.
8. Highland, R. G.; Brummer, J. G.; Crosby, G. A., "Redistribution of Energy Between Non-Equilibrated Electronic Excited Levels of Zinc(II) Mixed Ligand Complexes in the Solid State Via Heat Pulses", J. Phys. Chem., Vol. 90, 1593-1598, 1986.
9. Highland, R. G.; Crosby, G. A., "Determination of the Activation Barrier to Energy Transfer from  $\pi\text{-}\pi^*$  to Charge-Transfer Levels Via Steady State and Transient Luminescence Measurements on Bis(4-chlorothiophenol)(1,10-phenanthroline)zinc(II)", Chem. Phys. Lett., Vol. 119, pp. 454-458, 1985.
10. Fordyce, W. A.; Rau, H.; Stone, M. L.; Crosby, G. A., "Multiple State Emission from Rhodium(I) and Iridium(I) Complexes", Chem. Phys. Lett., Vol. 77, pp. 405-408, 1981.



Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 91321	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 92132	1

TECHNICAL REPORT DISTRIBUTION LIST, 051A

Dr. M. A. El-Sayed  
Department of Chemistry  
University of California  
Los Angeles, California 90024

Dr. E. R. Bernstein  
Department of Chemistry  
Colorado State University  
Fort Collins, Colorado 80521

Dr. J. R. MacDonald  
Chemistry Division  
Naval Research Laboratory  
Code 6110  
Washington, D.C. 20375-5000

Dr. G. B. Schuster  
Chemistry Department  
University of Illinois  
Urbana, Illinois 61801

Dr. J.B. Halpern  
Department of Chemistry  
Howard University  
Washington, D.C. 20059

Dr. M. S. Wrighton  
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Dr. A. Paul Schaap  
Department of Chemistry  
Wayne State University  
Detroit, Michigan 49207

Dr. W.E. Moerner  
I.B.M. Corporation  
Almaden Research Center  
650 Harry Rd.  
San Jose, California 95120-6099

Dr. A.B.P. Lever  
Department of Chemistry  
York University  
Downsview, Ontario  
CANADA M3J1P3

Dr. John Cooper  
Code 6173  
Naval Research Laboratory  
Washington, D.C. 20375-5000

Dr. George E. Walrafen  
Department of Chemistry  
Howard University  
Washington, D.C. 20059

Dr. Joe Brandelik  
AFWAL/AADO-1  
Wright Patterson AFB  
Fairborn, Ohio 45433

Dr. Carmen Ortiz  
Consejo Superior de  
Investigaciones Cientificas  
Serrano 121  
Madrid 6, SPAIN

Dr. John J. Wright  
Physics Department  
University of New Hampshire  
Durham, New Hampshire 03824

Dr. Kent R. Wilson  
Chemistry Department  
University of California  
La Jolla, California 92093

Dr. G. A. Crosby  
Chemistry Department  
Washington State University  
Pullman, Washington 99164

Dr. Theodore Pavlopoulos  
NOSC  
Code 521  
San Diego, California 91232

END

3-87

Dtic